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INVESTIGATION AND OPTIMIZATION OF
MICRO-OXIDATION TECHNIQUES EMPLOYED
IN GAS TURBINE ENGINE OIL
CHARACTERIZATION

Eilhard Jantzen, et al

Air Force Materials Laboratory

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FOREWORD

This report was prepared jointly by the United States Establishment and the Deutsche Forschungs-und Versuchsanstalt für Luft-und Raumfahrt E. V. (DFVLR) Institut für Flugtreib-und Schmierstoffe under the Mutual Weapons Defence Act--Data Exchange Agreement Annex No. (AF-66-G) 7405 (MWDDEA), with Dr. R. L. Adamczak, Chief, Lubricants and Tribology Branch (MBT), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, as Project Officer. The research was initiated under Project No. 7343, "Aerospace Lubricants", Task 734303 "Fluid Lubricant Materials". The results of the research described in this report cover work conducted during the period May 1967 through December 1970.

The report was submitted by the authors in April 1972.

This technical report has been reviewed and is approved.



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ABSTRACT

Rationale is provided which led to a modified oxidation-corrosion (O-C) test. This resulted from a cooperative laboratory program involving the Deutsche Forschungs-und Versuchsanstalt für Luft-und Raumfahrt E. V. (DFVLR) Institut für Flugtreib-und Schmierstoffe and the Air Force Materials Laboratory, Nonmetallic Materials Division, Lubricants and Tribology Branch. Test methods, apparatus, and procedures are described for use up to 800°F (427°C), a 20 milliliter amount of sample oil and a test time of 24 hours. The influence of various important parameters on oxidation-corrosion are presented. The reduction of the test duration to 24 hours was optimized. Oxidation/corrosion studies at several different temperatures and the resulting oil deterioration curves were shown to be meaningful from a minimum of 392°F (200°C) to a maximum of 700°F (371°C). The selection of the proper air flow was coupled with the reduced sample size as most appropriate for this work. The selection of high purity metal catalysts was justified. Analysis methods used in this work and their relative merits are discussed. Finally oxidation-corrosion data is presented on a few typical base stocks using this method.

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SECTION I

INTRODUCTION

Over the past several years, considerable effort has been expended in the development of better methods to evaluate gas turbine engine oils in the laboratory. Foremost of these efforts were those directed toward the various procedures for determining the oxidation and corrosion tendencies of aircraft gas turbine engine lubricants. The importance of this type degradation must still be considered because the predominant trends in future air-craft propulsion will be concerned with higher thrust to weight ratios and increased inlet air temperatures which result in lower sump volumes and higher thermal and oxidative stresses on the oil. Accompanying this is the continuing intimate contact of the fluid in thin film or droplet form with air in the presence of the various metals of engine construction. The basic philosophy of this test work then was to evaluate liquid lubricant deterioration at elevated temperatures in an oxidizing atmosphere with and without metals present.

Previous investigations have resulted in the development of many forms of oxidation corrosion test apparatus, methods, and procedures. For one reason or another they have not met the specific test conditions and procedural requirements are necessary to best evaluate oxidation-corrosion degradation of a gas turbine engine oil. Many of these oxidation-corrosion tests performed today within various industrial and governmental organizations are summarized in Table I.

Additional oxidation-corrosion tests with which the Lubricants and Tribology Branch of the Air Force Materials Laboratory became involved over the past several years are critically summarized below since they are relevant to this experimental work.

One of the latest oxidation-corrosion test methods (L-53-) evolved from Coordinating Research Council efforts is included in the latest Air Force high temperature gas turbine oil specification, MIL-L-27502. This is categorized as a full scale test utilizing 200 milliliters of fluid,

TABLE I
OXIDATION-CORROSION TESTS FOR AIRCRAFT FLUIDS

Method Identity	Method Number	Oil Sample Size ml.	Air Flow l/hr.	Aging		Metal Specimens	o/c Tube Dimensions		Air Inlet Tube, Diameter mm	Specification Usage
				Temp. C	Time hr		Length mm	Diameter mm		
Corrosion & Oxidation Stability of Light Oils	FTMS 791a 5308.5	100	5	175 204 121	72	Cu, Mg, Al Ag, Steel	500	50	6.0	MIL-L-7808 MIL-L-23699 MIL-L-6081
Oxidation-Corrosion Test (Sunburry Beaker Test)	---	400	0	140	22	Cu/Cd	200	100	Agitated 400 rpm	DENGRD 2487 DENGRD 2497
Oxidation Test	IP 48/67	40	15	200	2x6	None	250	25	4.8	
Oxidation-Corrosion Stability (Pratt & Whitney)	---	100	5	220 175	48 72	Same as FTMS 5308.5	500	50	---	PWA 521 B
Oxidation-Corrosion Stability (Allison)	---	100	5	175	72	Same as FTMS 5308.5	500	50	---	EMS 35-H
Oxidation-Thermo- Stability (Rolls Royce)	RR 1001	50	15	150 min.	72 +	None	250	25	5.0	---
Oxidation-Thermo- Stability (USSR)	GOST 981-4	30 g.	3	150 175	14/ 50	---	---	---	---	---
Oxidation-Corrosion Stability (Southwest Research Institute)	---	200	130	238 260	18 to 48	Ti, Al, Ag, M-10, 301, Mild Steel, Mg	500	22	2.0	---
Oxidative Stability of Gas Turbine Lubri- cants with Metals (USAF)	CRC L-53 -368	200	10	220 240	48	Al, Ag, Cu, Mild Steel, Mg, Ti	500	50	6.0	MIL-L-27502
Oxidation-Corrosion Stability (MBT-WPAFB)	---	20	10	204 or higher	24	Al, Ag, Ti, Mild Steel, M-10, 301	500	22	2.0	---
Oxidation-Corrosion Stability (DFVLR,	---	20	10	204 or higher	24	Same as above	500	22	2.0	---

10 liters per hour of air, seven washer type metal specimens, and contains provisions for sampling and testing used fluid during the 48 hour test period. Metal weight changes and appearance, evaporation loss, viscosity change, neutralization number change, and volume of sludge are determined in this method and others described below as a measure of fluid deterioration. The large sample size (200 ml) and frequent sampling of the fluid does not lend itself to the small developmental volumes of fluid which are frequently available as samples for characterization.

Federal Test Method Standard 791a, Method 5308.5, "Corrosiveness Oxidation Stability of Light Oils (Metal Strip)" utilized to evaluate synthetic ester type fluids and referred to in specification MIL-L-7808, also requires a large sample of 100 milliliters and standard "macro" glassware. This is still hardly suited to the quantity of developmental fluids available. This method employs the old style metal squares tied together with twine, a reflux condenser, and air flow at a rate of 5 liters per hour. Standard used oil tests and metal specimen examination are used to evaluate the test fluid.

In 1955 the Lubricants and Tribology Branch introduced a one-fifth scaled-down version of the apparatus used in Federal Test Method Standard (FTMS) 791a, Method 5308.5 for evaluating petroleum base hydraulic fluids. It used a 20 milliliter sample, one liter per hour air flow, washer type metal specimens, and a reflux condenser. However, it was believed by many researchers concerned with development of advanced gas turbine engine oils that this oxidation corrosion method was not severe enough.

In this same area, the Celanese Chemical Corporation developed a large bench scale oxidation-corrosion test just prior to 1960. It employed an aluminum heating block maintained at 425°F, large scale glassware, a 250 milliliter sample, an air rate of 96 liters per hour, five metal squares, and used no condenser. Samples of oil were drawn every five hours over a thirty-five hour period and make-up oil added at the same intervals to equalize any overhead losses. The large sample size and the requirement for oil make-up were the principal objections to this procedure.

In 1960 a large scale oxidation corrosion test was developed by the Lubricants and Tribology Branch in cooperation with the Celanese Chemical Corporation specifically for evaluating MIL-L-9236 ester type fluids at 425°F to simulate bearing rig and jet engine operating conditions. Essentially the apparatus was similar to that now employed in the Federal Test Method Standard No. 791a, Method 5308.5 with the following exceptions: shortened oxidation tube and elimination of the condenser, increased sample size (250 milliliters), air flow from 36 to 48 liters per hour, and intermediate sampling and fluid make-up to replace evaporation losses. This method had the obvious shortcoming of "macro" sizing and was directed toward simulating a specific system environment and probably could not be extended to differentiate between other fluid classes exposed to other types of environments and/or operating conditions.

Wyandotte Chemical Company, under Air Force contract, took an opposite direction in test method development where a miniature scale rapid oxidation screening test was evolved for applications involving stable high temperature functional fluids. In this procedure, the glassware apparatus was miniaturized to accommodate 2 milliliters of sample, air flow of 0.5 or 2.0 liters per hour was used depending on the selection of mild or severe conditions, no metal catalysts were used, and a temperature of 500°F for 6 hours was maintained. The small sample size was a distinct disadvantage because, if an appreciable fluid loss was encountered, there was insufficient residual fluid to determine property changes that would indicate fluid deterioration.

For several years, Southwest Research Institute (SwRI), under Air Force contract, specifically sought to develop an apparatus and procedure for determining the oxidation corrosion characteristics of gas turbine lubricants in the 425 to 500°F temperature range and above. Procedures evolving from this work for 425 to 500°F utilized a liquid bath as a heating media and the 500°F and higher studies employed an aluminum block as a heat source. It was from this work that the CRC-L-53-368 oxidation corrosion procedure evolved and a Federal test method is being finalized. However, as in other bench scale tests, the primary objections to both SwRI tests were the macro-scale apparatus and the accompanying large test sample requirement (References 1 and 2).

SECTION II

DISCUSSION OF TEST METHOD DEVELOPMENT

To satisfy a need for a standardized oxidation-corrosion procedure, a cooperative development effort covering several years has been conducted between the Lubricants and Tribology Branch, Air Force Materials Laboratory and the Institut für Flugtreib-und Schmierstoffe of the German Research and Development Center for Aerospace EV (DFVLR). This cooperative effort was a natural undertaking because for many years the specialized laboratories of both countries had shown very similar test development programs and both parties agreed on the performance requirements of gas turbine engine oils. Before beginning actual work, it was first necessary to specify which of the individual parameters of the test procedures, based on past developments and future needs, should be incorporated into developmental efforts. These parameters were determined to be particularly time, temperature, air flow, sample size, and effects of metals.

In the previous summary of oxidation-corrosion test procedures it was seen that many differences in types and magnitudes of the controlling parameters occurred. One of the goals in this effort was to reduce test time. Long term testing has justification in that it helps establish basic information. However, for comparative investigation, service test monitoring, and quality control usage a shorter test period is sufficient in most cases. In this respect, the test time should normally be decreased, if possible, to 24 hours and in special cases to 48 hours. The trend appears to be in this direction already since all the current methods listed on Table I, with one exception, are run for 72 hours duration or less. In order to obtain a differentiation in fluid quality, a reduction of the time must in all cases be accompanied by an increase in severity of another test parameter such as temperature. Temperature under 200°C (392°F) are in this respect of little value. For the investigation of new lubricants which are thermally stable up to 371°C (700°F), temperatures between 300 and 371°C (572-700°F) are of more interest. In addition it is felt that evaluations of all previous and

current gas turbine engine oils at a single temperature leave something to be desired. That is, oxidation-corrosion tests would be of more value if they are conducted at three or four different temperatures and the analytical results versus temperature plotted to make oil deterioration curves. Oxidation-corrosion temperature conditions are selected initially to give viscosity change data in the range of 5 to 10 percent. Temperature conditions are increased in severity to a point where viscosity change data begin to depart from the initial values to about 30 percent. Finally the upper portion of the curve is developed by further increasing test temperature conditions so that they result in data changes in the neighborhood of 300 percent. In this latter range slight changes in the test temperature of 1°C to 2°C show great changes in viscosity of from 50 to 100 percent. This is shown later in Figure 11 where several chemical classes are compared. This temperature-viscosity change relationship provides the necessary information to limit the maximum test temperature. However, it is also the area in which the greatest disparities in data reproducibility occur. The knowledge, however, of whether an oil at a given temperature changes very rapidly or slowly can be determined utilizing this procedure. Also the question of whether the viscosity sharply increased or decreased or if the decomposition products are corrosive to certain metals and to what degree can also be answered. Airflows are another parameter where there are wide differences from test to test as shown in Table I, where they vary from zero to 130 liters per hour. It is therefore essential to consider the amount of air flow in relation to the other conditions. The reduction of sample size within reasonable limits must also be considered. It would allow greater flexibility in test application to quality control or lubricant service evaluations where minimum samples mean less make-up oil and thus better retention of used oil performance and characteristics. It also would permit characterization of experimental candidate fluids, which may at times have been recently synthesized at considerable expense and are available only in minimal quantities. The large number of oxidation-corrosion methods and apparatus contained in Table I are in themselves an increasing concern, since use of many procedures generates many results which cannot be qualitatively or quantitatively compared.

1. Test Apparatus and Procedures

The widely used oxidation-corrosion apparatus employing a heated glass tube containing a particular sample size through which air is introduced was employed in this test work. Temperature and air flow were held constant, dependent upon the selection of test conditions. The apparatus developed for this purpose consisted of a thermostated metal block with arrangements for temperature variation, air flow regulation and measurement and where necessary, devices for heating the air used in testing. The measurement and control arrangements were conveniently arranged in a control console. Figure 1 shows the overall construction of such an apparatus with two thermostated baths.

2. Thermostated Metal Block

The heating of petroleum substances with the aid of a metal block is generally required at high temperatures. This has the advantage, opposed to the limitations of thermostated liquids, of reduced maintenance, increased cleanliness and odor free operation. The temperature distribution is relatively constant. Control point swinging is evened through two point regulation with damping. Some disadvantages are relatively long heating and cooling times and a sluggishness to quick temperature changing.

For constant high temperature over the entire block, and shortest possible heating and cooling times, relatively small cube shaped metal blocks are employed. A further advantage of the smaller units compared to an individual large block, is that relatively larger temperature variance can be tolerated in each small block and therefore stoppage of essential work cannot occur with the failure of a single thermostat or regulator. Figure 2 shows the arrangement of one such thermostat with the metal block in the center and adequate insulation that is necessary to hinder heat losses especially above 300°C (572°F). The metal block consists of a high melting aluminum alloy. This material has an advantage over copper in that it is easier to machine, has a low weight and a favorable price. It can be used with safety to 427°C (800°F). The present gas turbine engine oil candidates lie in the range of 200° to

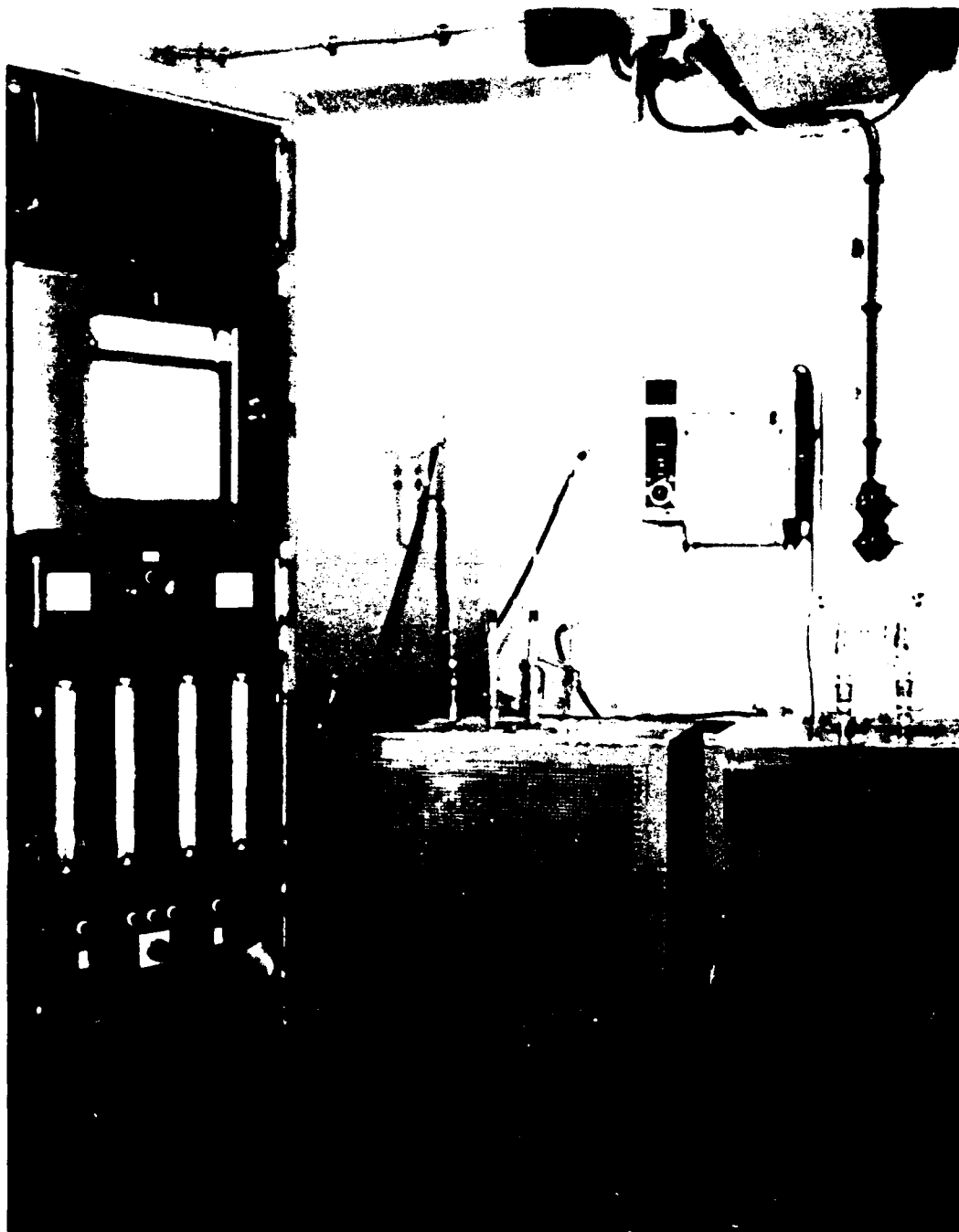


Figure 1. General View of the Apparatus

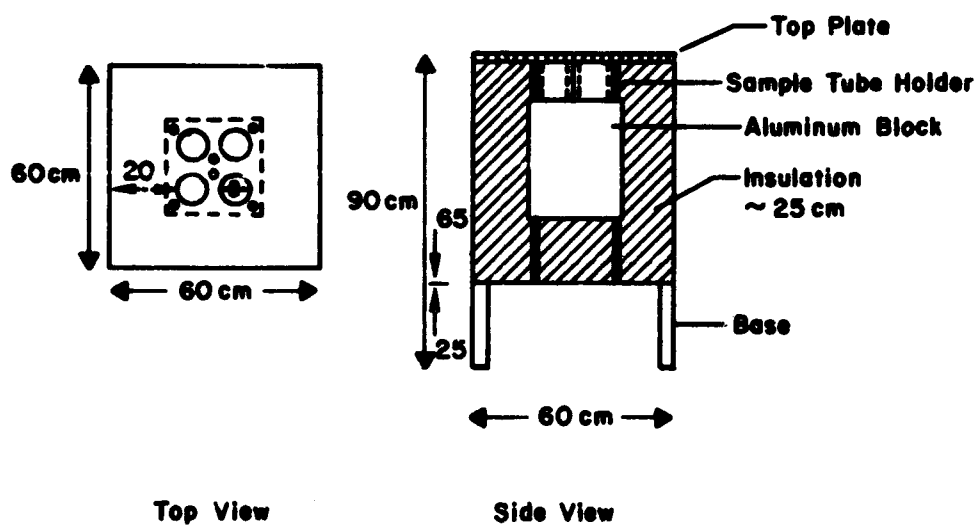


Figure 2. Cross Section and Construction of a Thermostated Metal Block

300°C (392 to 572°F) so that this material is sufficient for most purposes. If it is necessary to conduct oxidation-corrosion tests over 800°F (427°C) a copper block should be used. The thermal conductivity of copper is considerably better ($Al\lambda = 170$, $Cu\lambda = 300$).

The heat transfer from the block to the oil sample can be accomplished using air, sand, etc. or a low melting metal alloy. We have developed a method that shows several advantages. It consists of a brass tube that is spherically sealed at the bottom in which the aging tube made of glass is placed and the diametrical clearance between the tubes is about 1.5-2.0 mm. The space between the brass tube and the metal block is filled with a metal powder--for example aluminum. In this manner good heat transfer is achieved and comparatively easy access to and removal of the sample tube is accomplished. In case the glass tube breaks, the escaping oil is retained by the brass tube and is easily removed without turning off the entire apparatus. This also does not interfere with the other experiments in progress at the time.

3. Temperature Control, Accuracy, Calibration, and Recording

For the most constant temperature control over the entire metal block, an even distribution of the heating elements over the block is necessary. The order in the block and the switching steps are shown in Figure 3. Each side wall of the block has three heating elements of 250 watts and so switched that even heating in three switching steps is possible. The third heating step of 3750 watts is only necessary for the initial heating. After reaching the desired temperature, the first heating step with 1250 watts is sufficient to maintain temperatures in the neighborhood of 400°C (752°F). Under a temperature of 200°C (392°F) it is useful to have a reduction transformer in the line to reduce oscillation of the temperature. The temperature is controlled with a two-point controller. With this arrangement at full load (3750W), a temperature of 232°C (450°F) is reached from room temperature in about two hours (See Figure 4 and Table II). A further time of about one hour is required to bring the oil sample to this temperature using the previously mentioned brass and metal powder. If one uses silica gel instead of metal powder to transfer heat the time period is about doubled.

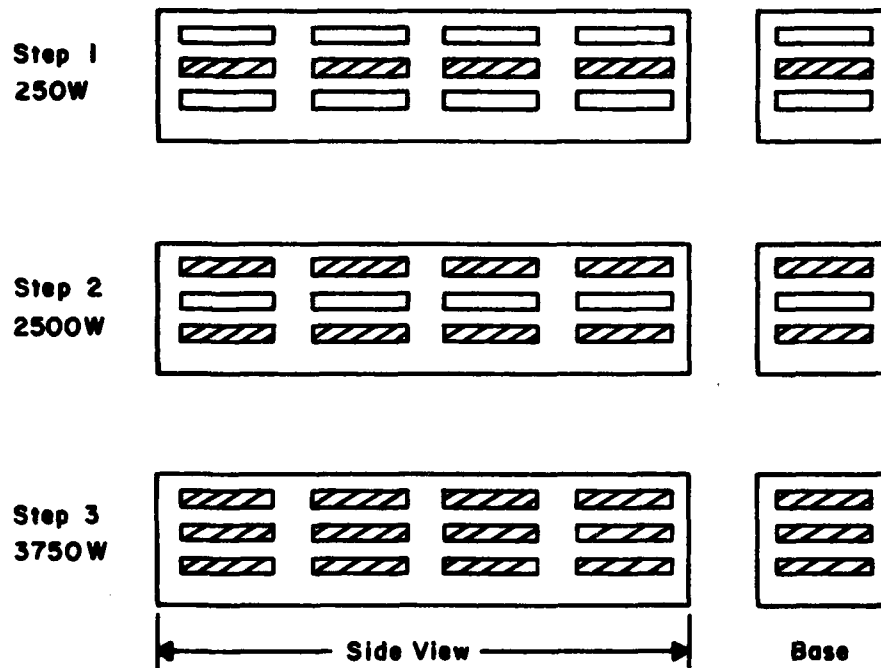


Figure 3. Placement of the Heating Elements in a Cube Shaped Metal Block

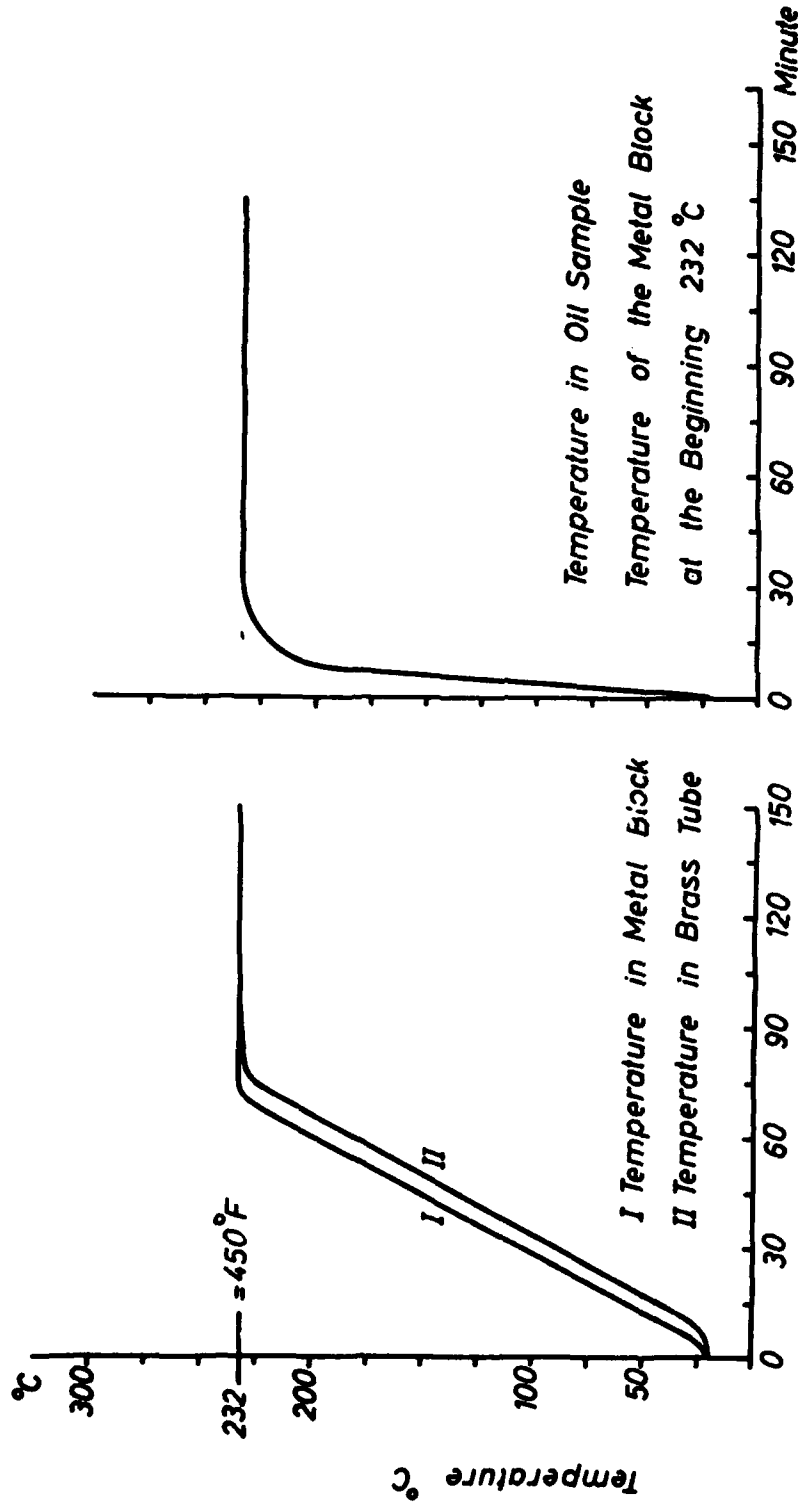


Figure 4. Heating Curves of the Thermostated Metal Block

TABLE II
TEMPERATURES OF OPENINGS IN METAL BLOCK BATH

Time (Min.)	Is Air On?	BATH TEMPERATURE 445 F										TEMPERATURE (F°) ON SAMPLE NUMBER				
		1*	3*	5	7*	9	-11	2	4	6	8	10	12			
0	No	443	444	445	444	443	442	79	79	80	80	80	82			
1.2	No	443	444	445	444	443	442	79	79	80	80	80	82			
2.4	No	443	444	445	444	443	442	79	79	80	80	80	82			
3.6	No	426	425	434	413	328	337	170	193	181	197	102	100			
4.8	No	419	416	427	409	333	343	258	273	248	284	143	140			
6.0	No	419	416	426	415	342	352	312	310	287	341	180	175			
12	No	431	428	433	437	383	392	403	395	376	426	315	308			
18	No	438	436	438	442	410	417	430	424	412	440	380	376			
24	No	441	440	441	442	425	430	438	435	427	442	411	410			
36	No	444	443	444	444	440	440	444	442	439	444	437	435			
48	No	445	445	445	444	442	442	445	444	442	445	442	441			
60	No	445	445	445	444	443	443	445	445	---	445	444	442			
72	No	445	445	445	444	443	443	445	445	---	445	444	442			
84	No	444	444	445	444	443	444	445	444	442	444	445	443			
85.2	Yes	444	445	445	445	445	445	445	444	442	444	445	443			
86.4	Yes	444	445	445	445	445	445	445	444	442	444	445	443			
87.6	Yes	444	445	445	445	445	445	445	444	442	444	445	443			
104	Yes	444	445	445	445	445	445	445	445	443	445	445	444			
122	Yes	444	445	445	444	445	444	445	445	443	445	445	444			
123.2	No	444	445	445	444	445	444	445	445	443	445	445	444			
124.4	No	444	445	445	444	445	444	445	445	443	445	445	444			
140	No	445	445	446	445	445	445	445	445	443	445	445	445			

Air Flow (liters/hour): (1) 20, (2) 1, (3) 10, (4) 0, (5) 20 (6) 1

*Brass tubes packed with aluminum grit in these holes.

An essential point is the consistency of temperature over long and short periods of time necessary for temperature regulation. The last mentioned is largely damped by the metal block and powder. The long term variation (over 100 hours) is with four samples in the apparatus where the maximum is $\pm 0.1^{\circ}\text{C}$ ($=\pm 0.05\%$ at $232^{\circ}\text{C} = 450^{\circ}\text{F}$).

For the temperature measurement, thermocouples or resistance thermometers are used which are calibrated to accurately determine temperature. For recording, a multi-point recorder is used with different colored inks and a chart 250 mm wide. In order to achieve a high resolution, a scale expansion of only 50°C , for example $200^{\circ}\text{C} - 250^{\circ}\text{C}$ is used.

4. Air Flow Regulation, Control, and Calibration

As previously mentioned, at higher temperatures the air flow rate becomes quite important. In order to maintain a high stability of the air flow through the tube an accurate and calibrated measurement device is necessary. With fluctuations in the compressed air system, it is recommended that several membrane pressure reducers be used in series or that a differential pressure regulator be used. Both techniques were used in this work whereby an airflow is obtained with practically no variation. The measurements are made on a rotameter that has a minimum scale of 10 mm per liter of air. A rotameter for the measurement of 15 liters per hour has therefore a length of 150 millimeters. The regulation is made with a needle valve.

In case the flow meters are not calibrated at the factory, the best method is the use of a soap bubble flow meter (burette). This flow meter measures the flow directly and it is easily obtainable commercially.

With a number of oxidation-corrosion experiments, the water content of the air enters into the results and it is therefore essential to eliminate the water completely or to set an exact limit on water content. With a normal air system the water level may exceed 1000 ppm. Silica gel and molecular sieves in drying towers can be placed in the line for drying but must be frequently tested and regenerated. A continual air

drying apparatus with molecular sieves or silica gel is a much simpler device. Values to 1 ppm are achieved with this apparatus. For short term tests it may be that values to 10 ppm are insignificant. The measurement of these low amounts of moisture can be accomplished with commercially available apparatus.

5. Glass Apparatus

In previous testing summarized earlier in this report and in Table I, much effort was reported on the form and dimensions of test apparatus. After studying this it was basically decided that a sample of 20 ml was sufficient for analysis as well as a reasonable amount of material to be supplied by the synthetic chemist. In FTMS 791a, 5308.5 and a number of other oxidation-corrosion tests, the length of the sample tube is 500 mm. This length was maintained. This guaranteed that the sample was always in the center of the metal block and at a temperature of 204°C (400°F) only a low oil loss by volatility or carry over from the air flow occurred. Consideration was given in regard to diameter of the tube that the metal discs for corrosion testing and their weight must not be too small. Therefore, a relatively large diameter to a short fluid level height was selected in order that only a small exchange surface existed between oxygen and the oil. An internal diameter of 22 mm was therefore selected for the tube which resulted in a 20 milliliters oil level of 55 millimeters. A condenser directly on the sample tube did not appear useful since this is not representative of the actual system. In an engine, generally a large amount of the low boiling decomposition products and the water formed are blown out by air through the bearing, so these products have only a small influence on the oxidation-corrosion of the oil. In order to attain the same relationship, an adapter is connected to the side of the sample tube that leads downward at 75° (see Figure 5) so that any condensate formed does not flow back into the tube.

The adapter has a female neck joint for a Liebig condenser and also another joint to connect a graduated flask for collection of the condensed portion (Figure 5). The gas inlet tube has a definite opening of 2 mm diameter at the bottom to produce definite sized air bubbles. Six mm

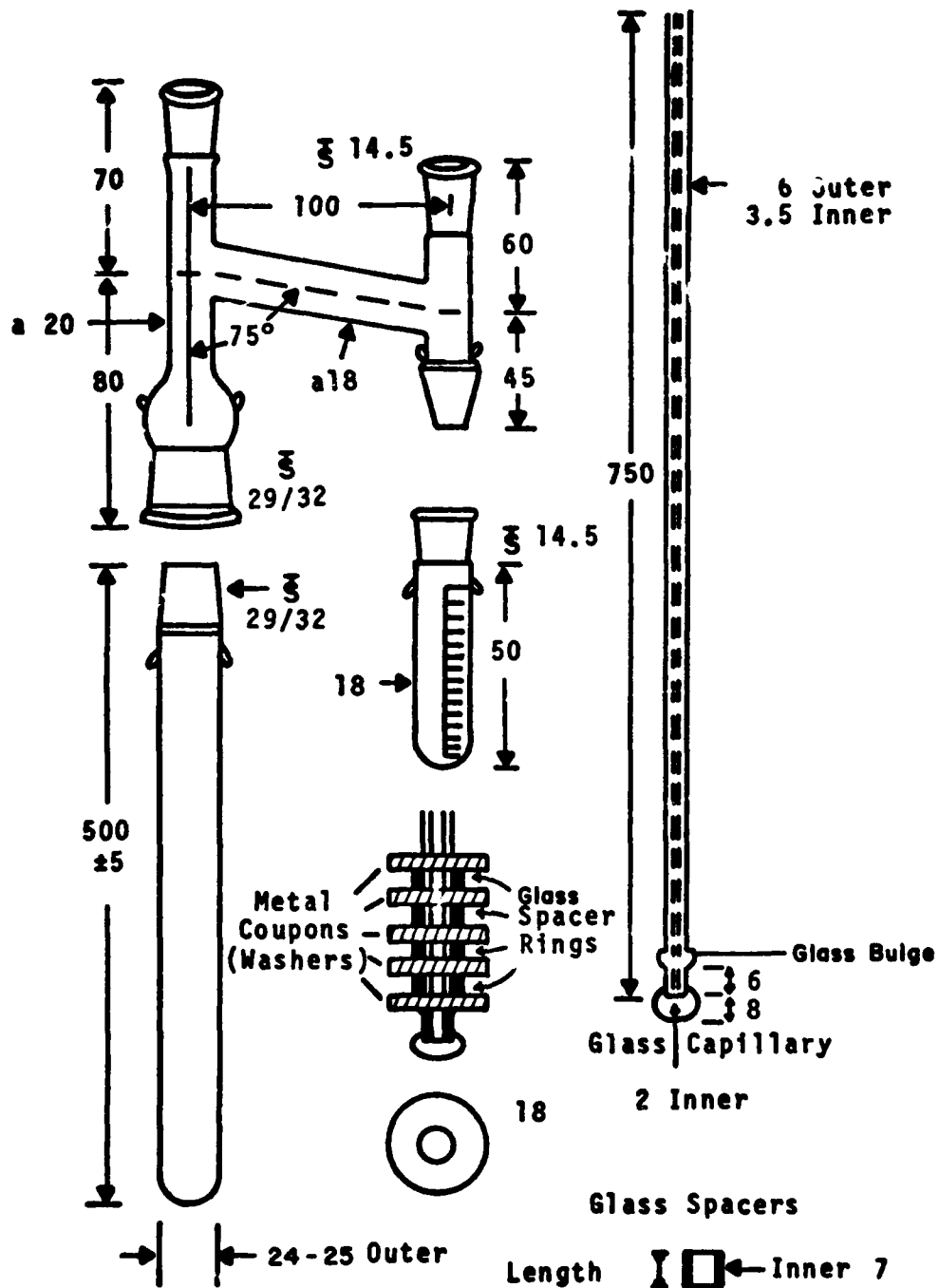


Figure 5. Glass Apparatus

from the bottom of the air inlet tube is a glass bulge to prevent the metal specimens from touching the bottom of the sample tube. Also a glass ring is fused to the capillary opening so that a distance of 8 mm from the opening exists. In this way the distance between the end of the inlet tube and the bottom of the sample tube is held constant. The metal coupons are spaced with glass rings at 6 mm intervals. Measurements are specified in the appendix.

In cases where it is of interest to investigate the gaseous decomposition products, it is possible to trap them with a dry ice condenser.

6. Metals

For the use of metals in oxidation-corrosion tests there are two very different goals. Considering the oil, it is first interesting to note what catalytic effect the metal has on oil decomposition at high temperatures in comparison to only air (oxygen). From the metal viewpoint, interest lies in the determination of the corrosive action of the oil or the decomposition products deposited on the metal. These two different purposes require a different method of selection of the metals. For the investigation of the catalytic effect a high purity material is useful in order to eliminate undefinable effects of alloy materials. In the investigation of corrosion, it is important to use alloys that are normally used in turbines.

An essential question is also whether four or five different metals or several coupons of the same alloy should be tested simultaneously. In the investigation of catalytic influences, in every case, only one metal should be used but in the investigation of corrosion different metals in the same oil sample can be used to determine synergistic effects on each other. The separation of the metal specimens with glass separators as shown in Figure 5 has proven useful.

Further, sufficient distance must be maintained between the outside of the metal disks and the sample tube so that when air flows through the tube the disks are not forced upward. With a tube of $22 \text{ mm} \pm 1 \text{ mm}$, a diameter of 18 mm for the specimens was established to maintain an adequate clearance.

7. Oil Sample Size

The various oxidation-corrosion tests use very different sample sizes. A few "Bench-Scale" tests (References 3 and 4) report amounts of 200-250 ml. The test under FTMS 791a, 5308.5 uses 100 ml of oil; while a Russian publication for testing of gas turbine oils (GOST 981) requires 30 grams of oil.

For quality control of commercially available gas turbine engine oils, an amount of 100-200 ml per test appears adequate. In research and development laboratories the pure production of large amounts of synthetic products is bound by cost, availability, and time factors so that, in this aspect, the smallest possible sample size is desired. Considerations previously reviewed in this report and testing have led to fixing the oil sample size at 20 ml. Through use of the previously described apparatus, good reproducibility is obtained. Even with a loss of one-third of the sample through volatility and decomposition, enough sample remains for viscosity measurements and acid number determinations. The analysis can be accomplished with losses of 50-60% if semi-micro-capillary Ubbelohde viscometers are used. The procedure used throughout this cooperative study appears in the Appendix.

SECTION III

INFLUENCE OF THE VARIOUS PARAMETERS ON THE RESULTS

In order to separate the influence of the individual parameters on the results they were individually evaluated using a turbine oil. With such experiments, it must be considered that favorable results are not in every case representative of what will occur under actual operating conditions but rather they may be attributed to too mild of investigative conditions. More severe conditions can show considerable differences that lead to other conclusions.

Property changes of gas turbine engine oils (GTO'S) based on esters have a characteristic relation to temperature increases in direct contradiction to oxygen (air) changes. Up to a certain temperature, very little change is noted. Above this temperature, the change is at first still insignificant and then a slight further temperature increase gives a sharp alteration of the properties of the sample. In Figure 6, curves of two typical turbine oils and a basestock, after oxidation-corrosion tests, are shown. Viscosity of the oil is plotted versus temperature after oxidation-corrosion testing. From 200°C (392°F) onward, the turbine oils began (under the above conditions) to show a definite increase in viscosity; so that after 24 hours at 218°C (425°F) a definite differentiation is possible. It is clear from the curves that at temperatures under 180°C (356°F) and maintaining other parameters constant, only a small change of viscosity occurs in the tested turbine oils. With the base stock, clear changes are noted already at 150°C under the same conditions. Since the decomposition rate with increasing temperature increases sharply and exponentially, the highest possible temperature which can be tolerated by the turbine oils is 232°C (450°F). Using these data it is useful to evaluate these turbine oils with ester base stock between 182.5°C (360°F) and 232°C (450°F) at three different temperatures in order to make it possible to plot meaningful oxidation-corrosion curves.

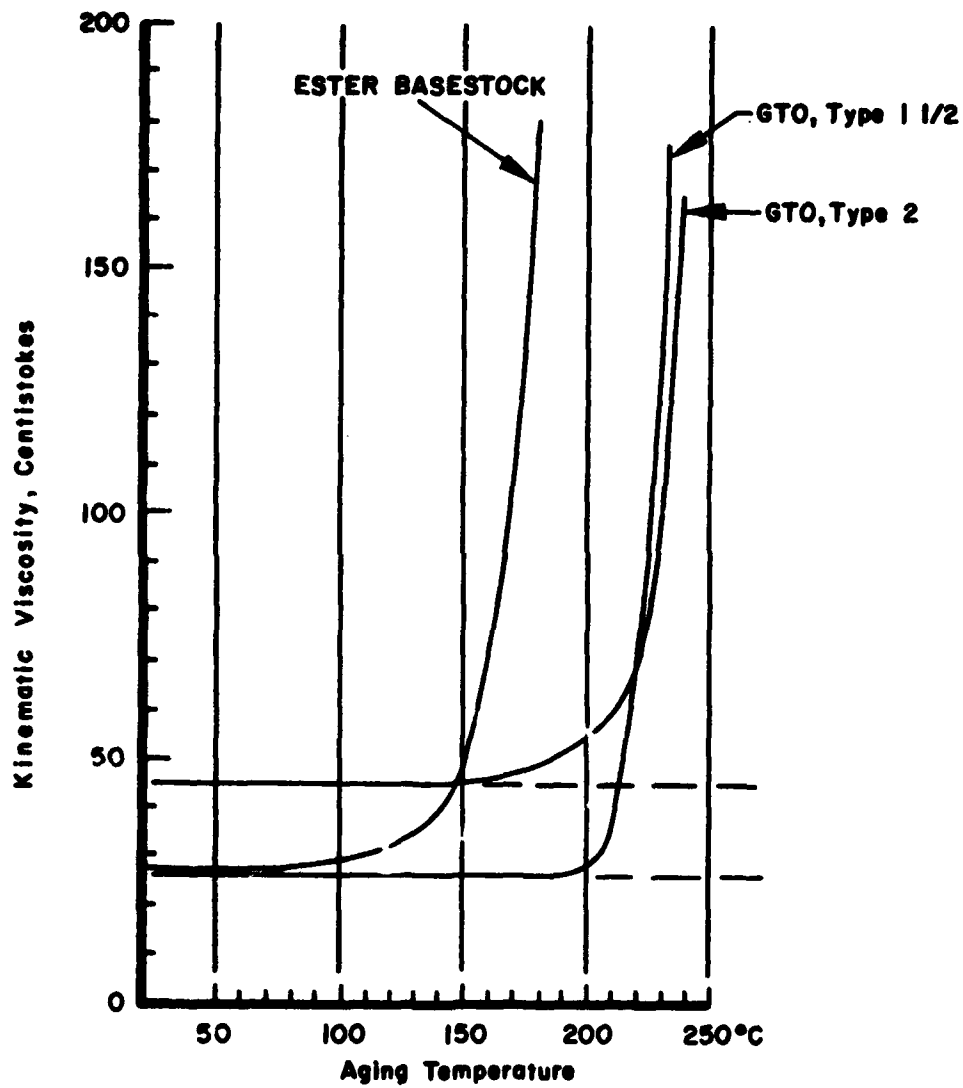


Figure 6. Influence of Temperature on Oil Deterioration

In most cases an oxidation-corrosion test time of 24 hours would be of considerable interest, so that in a relatively short time period, keeping in mind the goal of temperature differentiation, evaluations including three separate temperatures must be increased within the temperature ranges that are normally encountered in use. Correlation of test results with the condition of oils taken from all influencing factors and oil alteration are known.

Approaching operating practice is achieved through lowering or equalizing the oxidation-corrosion temperature to the practical operating conditions. With this comes an accompanying increase in test time. Such mild conditions can lead to wide differences in results. Experiments were conducted with the time period extended to 192 hours (8 days). Consideration was given to sample size. Should one age a large amount in a single container and from this draw samples at various times or use smaller amounts in many containers under the same conditions and draw them out at different time periods? The first way has the disadvantage that after each sample removal the oil/air ratio has been changed. On the other hand, in individual test tubes the relationship remains constant. Tests using multi-containers must be run with great care so that all of them are run at the same temperature, with a constant and equal amount of air. Figure 7 shows the results of testing over extended time periods and was accomplished using multi-samples withdrawn over various periods of time until the viscosity reached 200 centistokes at 37.8°C (100°F). The viscosity increase of the test oil can be determined by extrapolation. Increasing the time from 24 hours to 192 hours (8 days) makes it possible to decrease the test temperature from 232°C (450°F) to 190°C (375°F). Another evaluation method makes the exponential time influence clearer (Figure 8). This is the temperature where 100% viscosity change occurs when plotted versus test time. A 100% change was selected since this value is considered high for aircraft operations. The curve in Figure 8 shows clearly how strongly the temperature enters in the deterioration of the oils. Below a certain temperature (perhaps characteristic for each oil) the viscosity increases very slowly. If

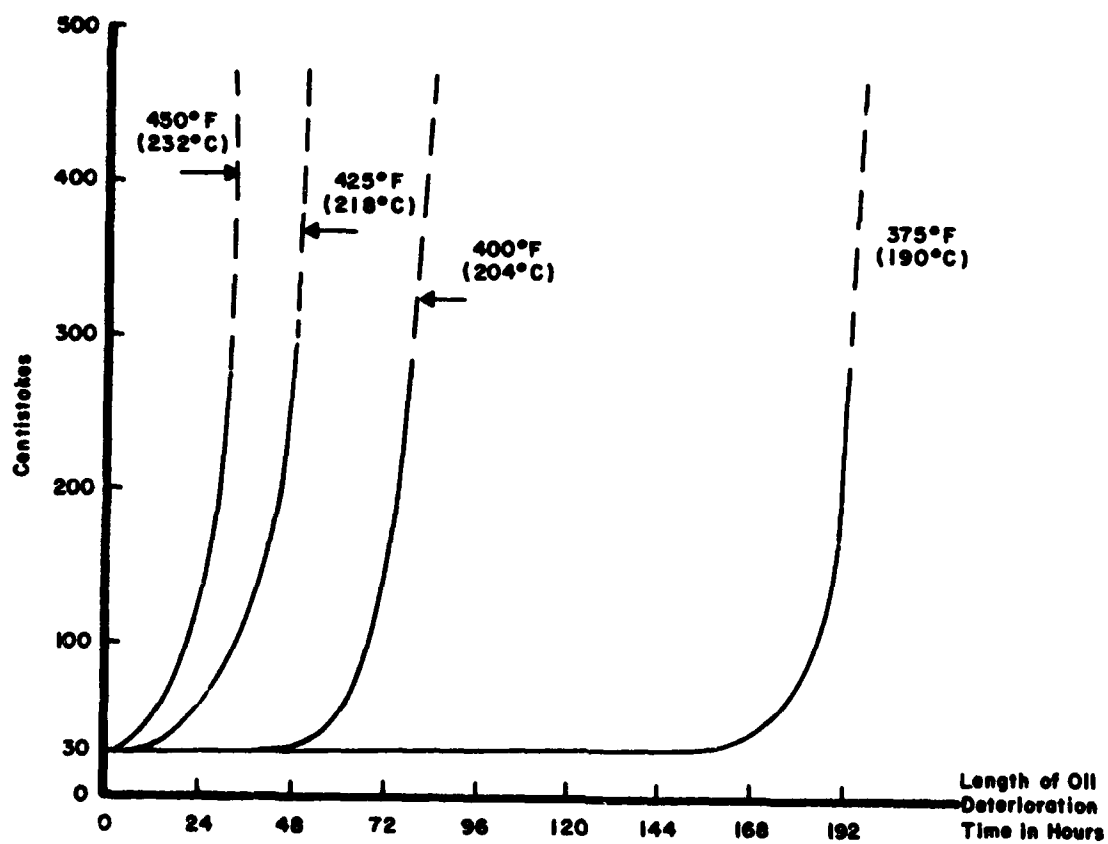


Figure 7. Influence of Temperature and Time

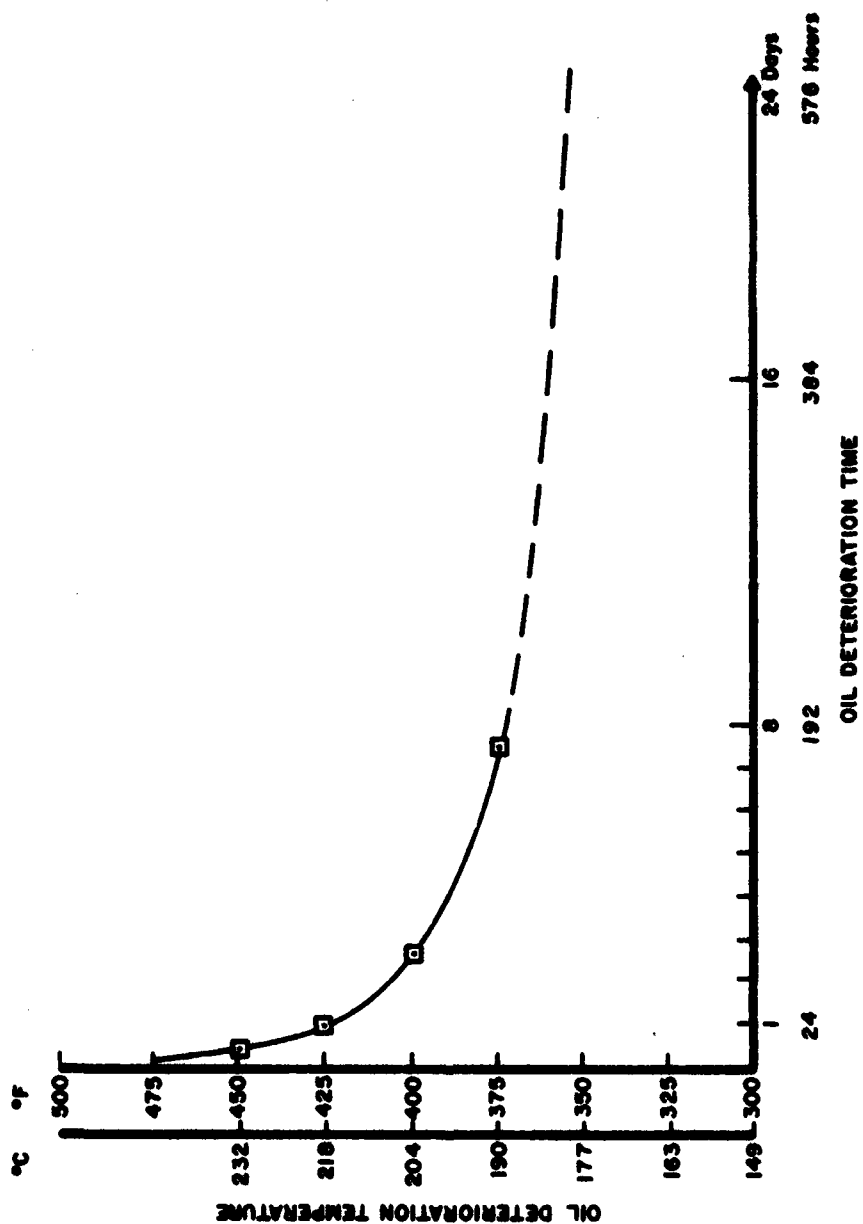


Figure 8. Oil Deterioration Temperature for 100% Viscosity Change

this temperature is exceeded (here 204°C (400°F), a sharp increase in viscosity occurs in a short period of time. Therefore, a supplementary long term test of an oil, for example, over a total of 24 days, with suitably lowered temperature can possibly give a good insight into the expected life of a turbine oil.

The influence of the amount of air on oxidation-corrosion stability of oils was investigated. As could be expected in this area, it was found that varying the amount of air had considerable effect on oxidation of an oil. It was found, for example, that an increase in air flow gave a sharp increase in the rate of deterioration as indicated by an abrupt increase in viscosity (Figure 9, Curve A). This indicates that for reproducibility of results a precise and constant air flow is necessary. Favorable air flow ranges are shown in Figure 9. For oxidation-corrosion test of 24 hours between 200 and 250°C (392-482°F), air flows of 5 liters per hour are too low to show a pronounced effect, while an air flow of 20 liters per hour provides extremely severe oil deterioration. Therefore, the most favorable air flow range is 10-15 liters per hour. Independent of this test work, Rolls Royce developed Method 1001 (Reference 5) and IP Standard 48/67 tests which give similar results. Both methods use 15 liters of air per hour and use sample sizes of 50 and 40 milliliters, respectively. In view of our relatively smaller oil amounts of 20 milliliters, we have standardized on an air flow of 10 liters per hour.

With increasing temperatures the catalytic influences of metals on oil stability increases in importance. In this area there are few published useable results, since most investigations were concerned with corrosion effects of the oil on the metal. These tests followed the normal pattern of using a number of different alloyed metals used in engine construction, which are then tested in the same oil sample. Other tests use only one metal so that no insight into the influence of various metals on the oil is possible. The procurement of a series of metals of extremely high purity, particularly in the form of thin sheets (normally used in these type procedures) is difficult. A technique was devised

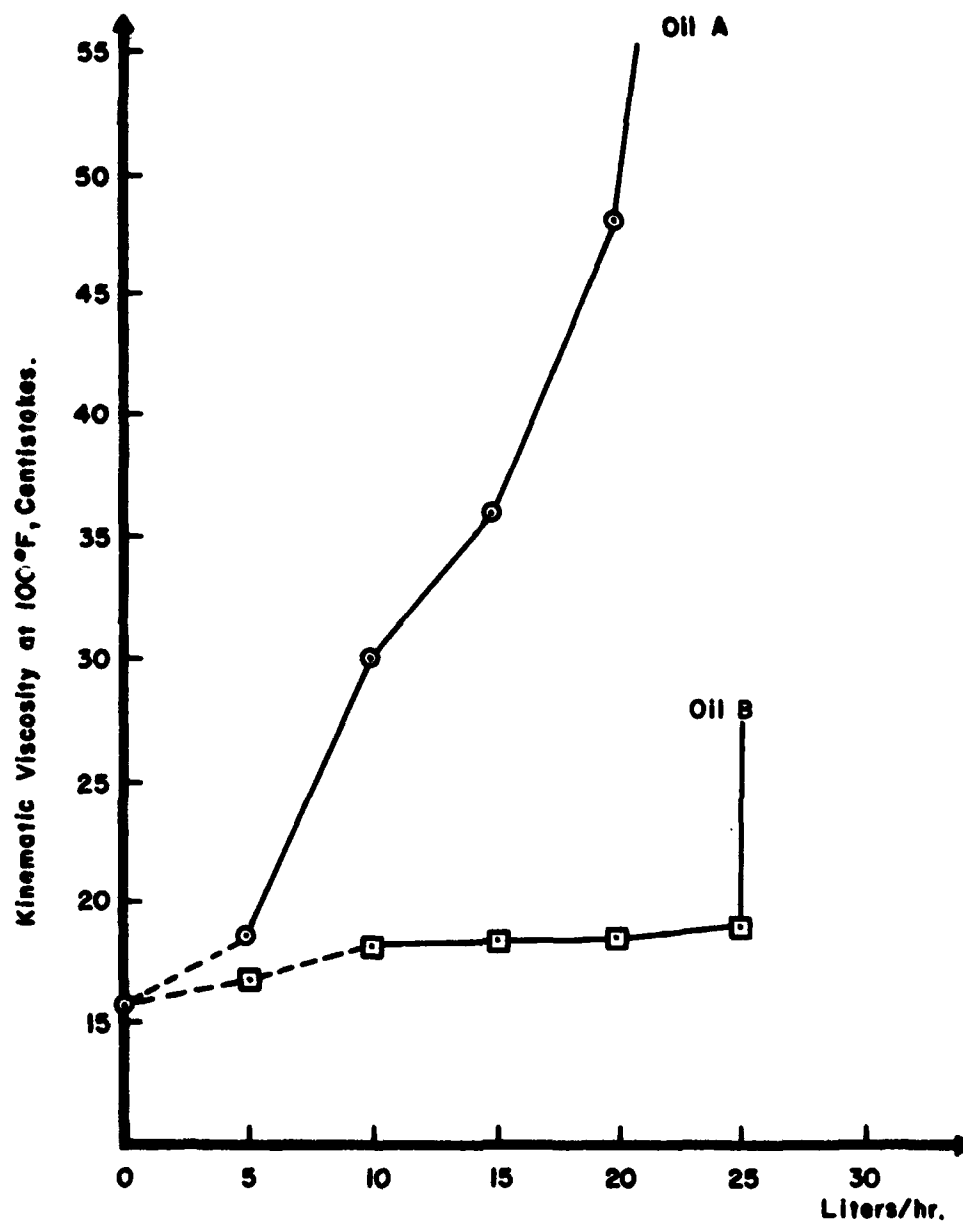


Figure 9. Influence of the Amount of Air Flow

which partly overcame these difficulties. Approximately 100 μ thick layers were electroplated from solutions of high purity metal salts onto the test specimens. First results with extremely pure copper, cadmium, and lead showed strong and different catalytic effects. Experiments with lead gave complete decomposition of the oil (Table III). Large differences in the amount of gaseous decomposition products was also observed.

Previous work has been reported in relation to the effect of humidity of air on oxidation-corrosion testing of oils (Reference 3). Expected results go hand in glove with the test conditions, oil type, and additive formulation. The results of Cuellar and Baber have shown that an increase in relative humidity from 0 to 50% gave a considerable decrease in the viscosity and acid number increases, also the weight losses were smaller. A clarification of these relationships is not possible especially since all oils do not show similar effects. The largest changes lie in the range between 0 and 50% relative humidity. It appears therefore useful to keep the air humidity as low as possible.

TABLE III
OIL DETERIORATION OF ESTER BASE STOCK*, TESTED WITH METALS
24 HOURS AT 200°C, 10 LITERS OF AIR PER HOUR

	Without Metals	Copper (99.9% pure)	Cadmium (99.9% pure)	Lead (99.9% pure)	Fresh Oil
Appearance and Color	homogeneous dark brown	homogeneous dark brown	nonhomogen. layer dark brown	nonhomogen. layer dark brown	Water Clear
Viscosity at 100°F, cs	144.2	----	not measurable since nonhomogeneous		11.75
Neutralization No. mg KOH/g	15	----			0.01
Evaporation %	14	10	7	17	-----
Distillation Loss %	1	0.5	0.8	5.0	-----
Weight Change of the metals mg/cm ²	-----	6	23	60	-----

* Trimethylolpropanheptanoate

SECTION IV

DETERMINATION OF STABILITY CHANGE

The change in the oil can be determined by several analytical methods. It must be considered that the results allow different conclusions that depend on which property change of the oils was determined with the appropriate methods. It appears that several methods give only an average value of the change. For example, the viscosity, above all, shows change in molecular size. In most cases useable results can be attained using normal procedures. Acid number, gas losses, and viscosity begin to change at the same temperature (See Figure 10). From this temperature the amount of liquid distillation and gaseous products also increase (if only by a small amount). It is our opinion that in determining the deterioration of ester oils the acid number is the most significant. Other methods should be reported for the record.

Figure 11 presents the oil deterioration curves of some typical oils varying widely in chemical structure. The oil deterioration curves show the percent viscosity change versus the deterioration temperature from 100 to 450°C (212-842°F). The test conditions and procedures were the same as those previously mentioned in this report. Between 140-180°C (284-356°F) lies the oil deterioration temperature range of a tri-ester base stock (ELO 66-73). At 350°C (662°F) is the deterioration temperature of the polyphenylethers (5P4E, isomeric mixture) and between 400-450°C (752-842°F) are the perfluorinated compounds. The various chemical structures are sharply contrasted under these operating procedures. A large difference is noted between a base ester oil and a formulated oil as indicated by the steepness of the slope of the curve. Therefore, it would appear possible to determine the small differences caused by differences in additive activity by the use of these curves.

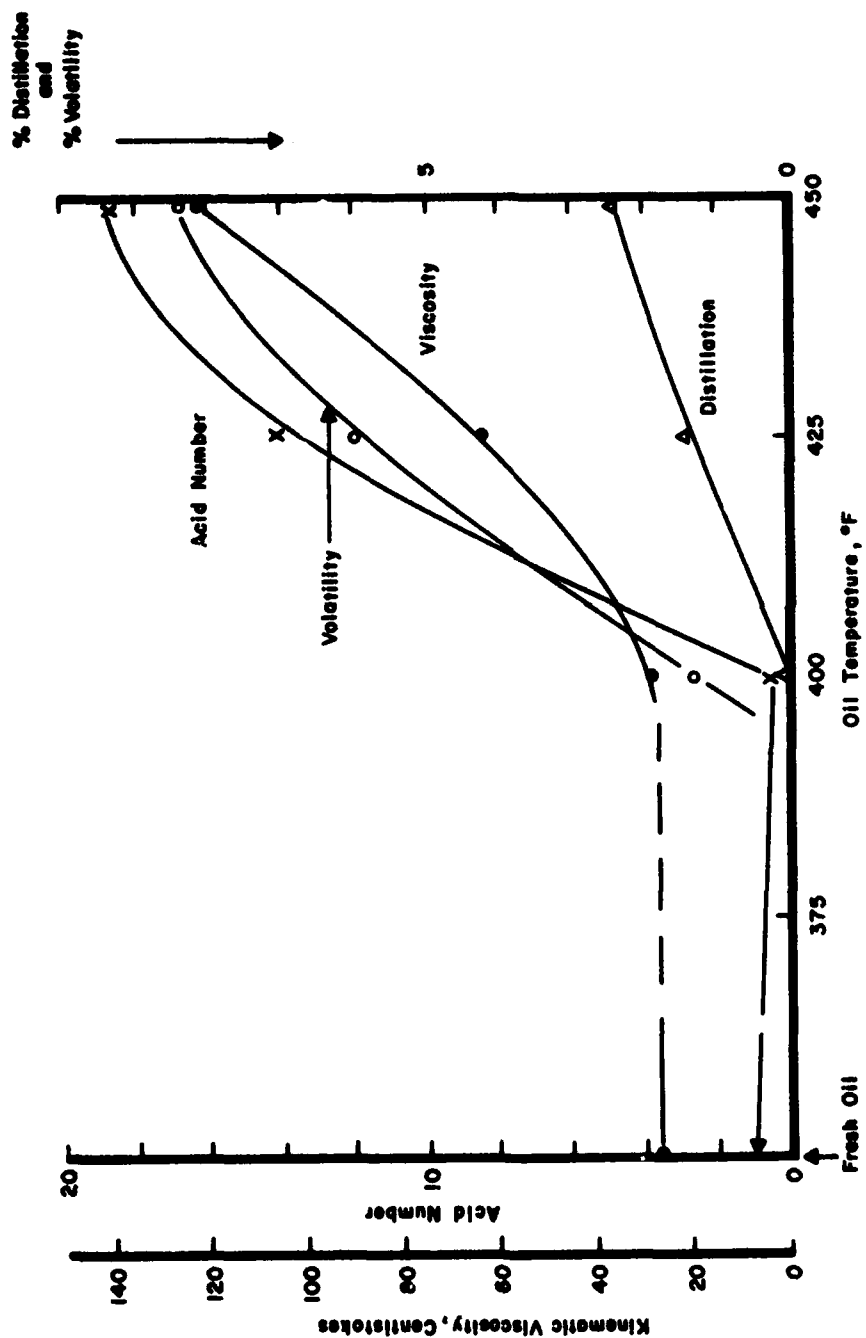


Figure 10. Relationship of Viscosity, Acid Number, Distillation, and Gas Losses to Oil Deterioration Temperature

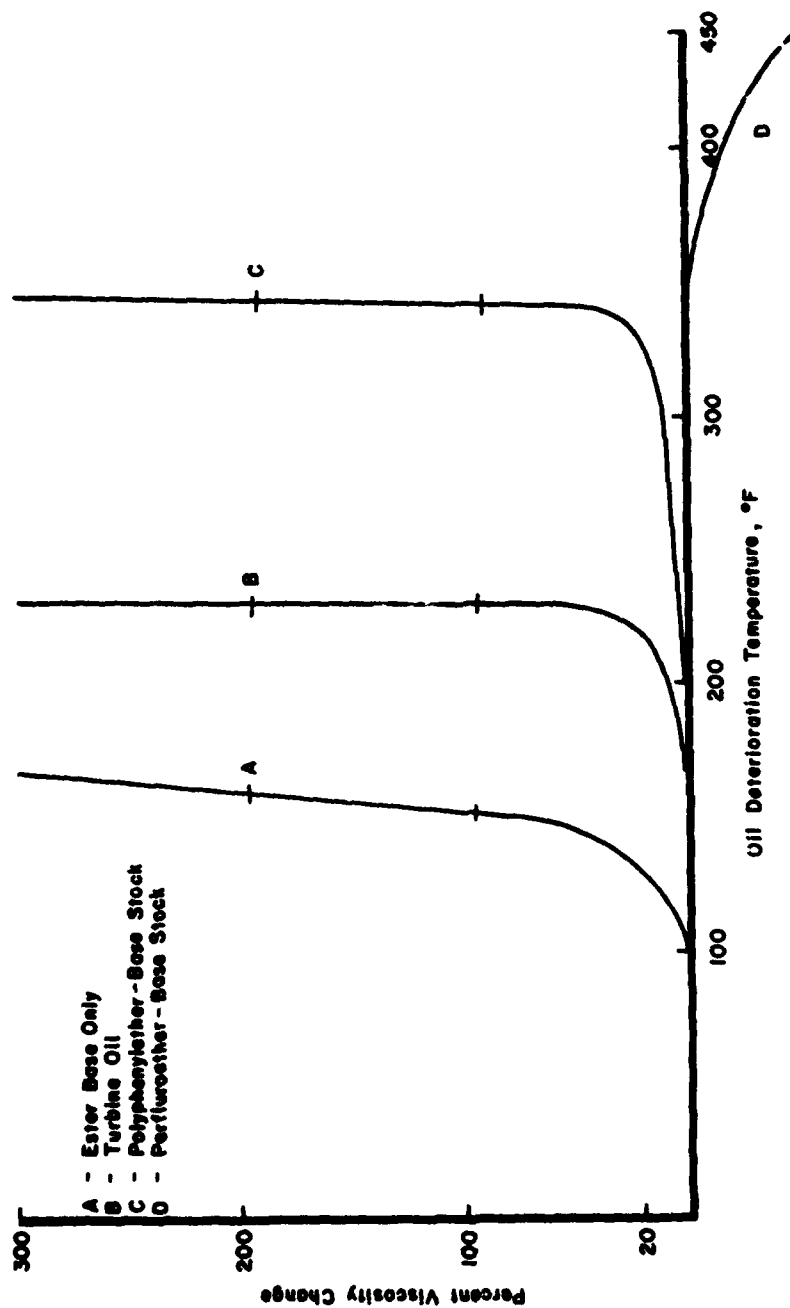


Figure 11. Change of Viscosity with the Oil Deterioration Temperature for Different Fluids

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

The study shows the continued importance of the oxidation-corrosion test in evaluating gas turbine engine lubricants. It would appear that the use of the microglass apparatus and the control of other test parameters, such as time, temperature, air flow, and metal specimens gives high accuracy of results and allows for great flexibility of the test tool in evaluating minimal quantities of experimental fluids in quality control or in lubricant service test applications. The use of oil deterioration curves plotted from kinematic viscosity and temperature can aid in indicating fluid decomposition levels and to differentiate between formulated gas turbine engine oil types and base stocks of varied chemical compositions.

It is recommended that future work in this area be continued on a cooperative basis. Such research and development efforts will be concentrated in studying chemically pure base stocks (esters), utilizing the above mentioned parameters incorporated into a standard method. Extracting ultimate performance characteristics from this chemical class of materials will demonstrate whether or not they will satisfy the short term goals imposed by propulsion demands of the immediate future which require fluids spanning the temperature range of -40°F to 500°F. The high temperature limitation is synonymous with oxidation stability. Since previous work in this area has indicated that this type stability is at least 100°F below the determined thermal stability of neopentyl and pentoerythretol based esters it would appear that the high temperature goal could be reached through the astute use of additive components. This oxidation-corrosion procedure will be used as a basis for mechanistic studies that will better enable us to determine the most expeditious route to follow.

APPENDIX

LABORATORY TEST CONDITIONS AND PROCEDURE

Sample Size	20 ml at 20°C (68.0°F)
Sample height in sample tube	70 mm
Distance of the air inlet tube from the bottom	8 mm
Sample tube diameter	22 mm (inner)
Sample tube length	500 mm
Sample tube material	Pyrex or Duranglas
Air Flow	10 liters per hour \pm 0.1 liter
Humidity	10 ppm \pm 5 Max. (*)
Test Time	24 Hours
Temperatures	204°C (400°F) 218°C (425°F) 232°C (450°F)
Metal surface	No pits at 20 magnification
Metals	For first investigation of the corrosion behavior the following are suggested: (***) Silver 99.9% Aluminum 2024 Alloy Tool Steel M-10 Stainless Steel 301

*Beginning at start of air flow

**After screening tests at all three temperatures and drawing of aging curves by plotting temperatures vs viscosity or neutralization number and light transmission.

***For investigation of the catalytic effect of metals, under varying conditions, a complete series of metals must be included such as Al, Fe, Cr, Ag, Cu, Sn, Ni, Pb, Ti. Their purity should be at least 99.9%.

PROCEDURE

- a. The metal block is heated to the desired temperature ($\pm 0.1^{\circ}\text{C}$)
- b. The empty weight of the glass apparatus (distillate flask separately) is determined (excluding condenser) (error $\pm 0.1\text{g}$).
- c. Fill the sample tube with 20 ml (± 0.2 ml) of test oil and redetermine the apparatus weight.
- d. The glass apparatus is placed in the thermostated metal block when temperature is constant and the condenser attached.
- e. Fifteen minutes after placing the sample tube in the bath begin air flow.
- f. After 24 hours the air connection is removed and the sample removed and cooled in air.
- g. Thirty minutes after removal the tube is reweighed and fluid loss determined.
- h. Weighing of the distillate flask (distillate weight).
- i. After weighing, a viscometer is filled, and thermostated for 30 minutes, then measure.
- k. Finally measurements of the acid number (*) and the light transmission.

Cell thickness 1 mm, wave length range 380-780 nanometers (nm)

If the experiment is done with metal specimens, these must be first polished, cleaned, dried and weighed. After the end of the experiment the specimens are washed with benzene, dried, and reweighed.

*Potentiometric method - ASTM-D-664

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